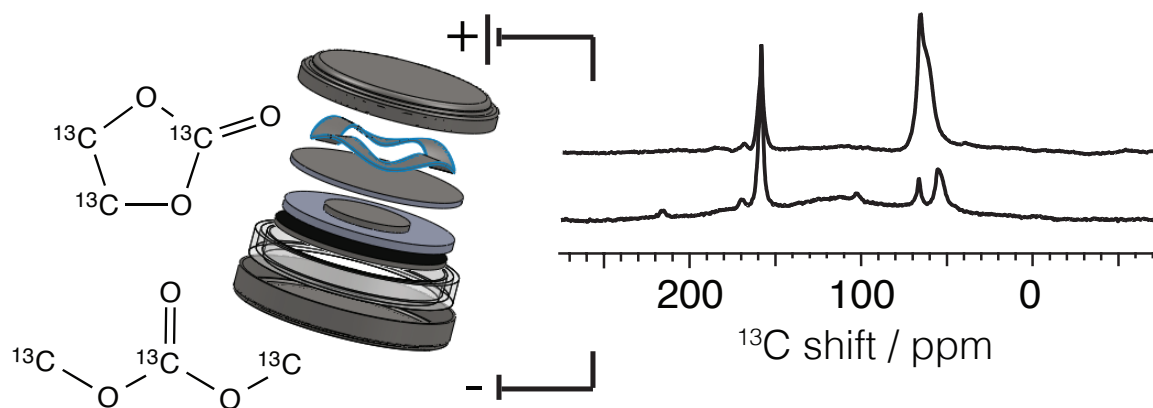# NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

P.I. Name: Clare P. Grey

University of Cambridge
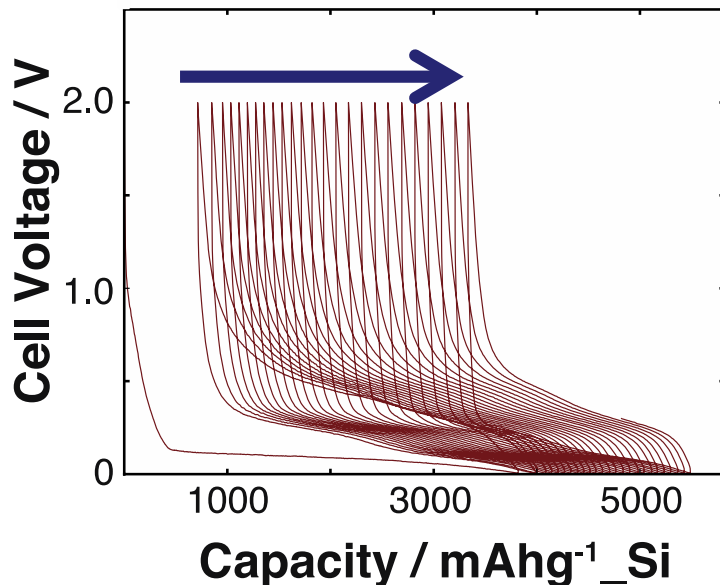
4/07/2016

Project ID
ES055

Overview

Timeline

- Project start date: 1/1/13
- Project end date: 12/31/16
- Percent complete: 80%

Budget

- Total project funding: $1.1M
- Funding received in FY14:
$ 277,954
- Funding for FY15: $ 283,936

Barriers

- Life (capacity fade)
- Performance (high energy density)
- Rate

Partners

- Brett Lucht (Rhode Island)
- Alexej Jerschow (NYU)
- Ram Seshadri (UCSB)
- Anton Van der Ven (UCSB)
- Stephan Hoffman (U. Cam)
- Andrew Morris (U. Cam)
- Dominic Wright (U. Cam)
- Erika Eiser (U. Cam)
- Cate Ducati (U. Cam)
- Paul Shearing (UCL)
- Peter Bruce (Oxford)

Relevance:

Overall objectives:
- Design a stable SEI
- Reduce overpotential (e.g., interfacial resistance, "structural hysteresis")
- Optimise performance of high capacity anodes and cathodes

Specific Objectives – March 2015-16

- Identify major solid electrolyte interphase (SEI) components on SI, and their spatial proximity, Li^+ transport through SEI, and how these changes with cycling (capacity fade)
- Extend to CEI
- Use recently developed in situ NMR/MRI metrologies to investigate Li (and Na dendrite formation), and the role that additives and different electrolytes play in controlling Li(Na) morphology.
- Develop new coatings for Si to reduce SEI formation
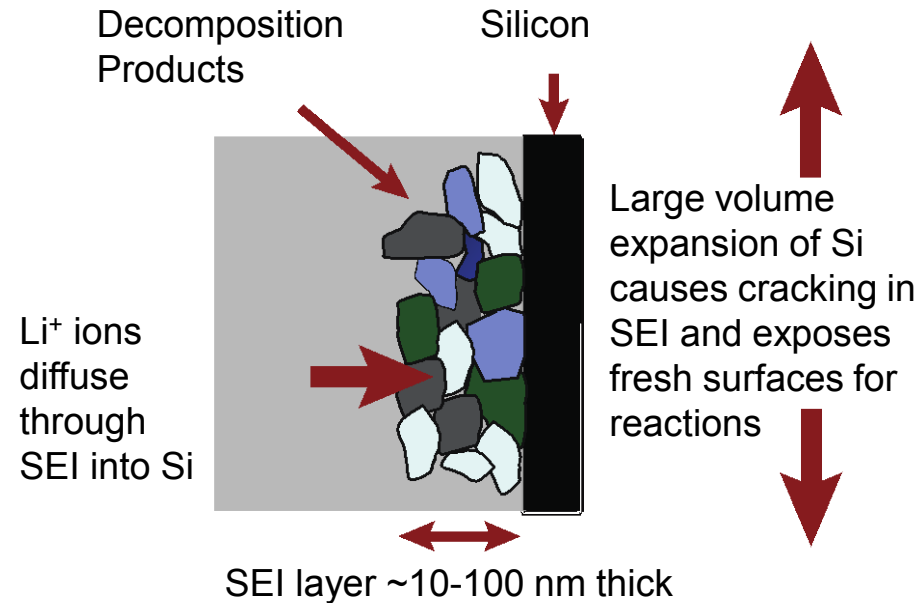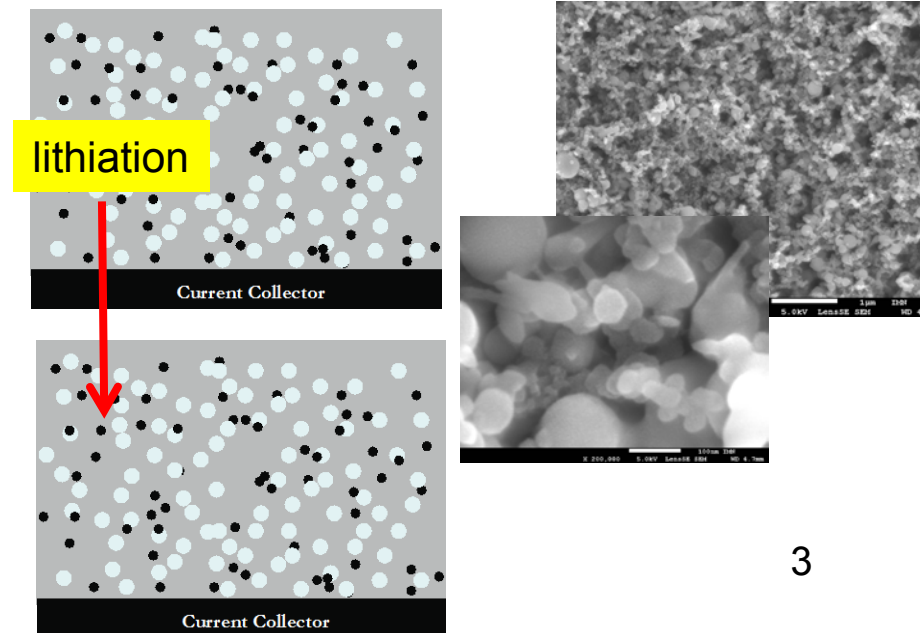- Use NMR methodologies to study beyond Li cathodes (Na, Li-air)

Decomposition Products

Silicon

Li^+ ions diffuse through SEI into Si

Large volume expansion of Si causes cracking in SEI and exposes fresh surfaces for reactions

SEI layer ~10-100 nm thick

Figure based on E. Peled et al. *J. Electrochem. Soc.* 144, L208 (1997)

lithiation

Current Collector

Current Collector

3

Milestones

2014

Q2. Identify differences in Si SEI after one and multiple cycles. (3/31/15)**; paper submitted and under review**

Q3. Identify major organic components on the SEIs formed on high surface area carbons by NMR. (6/30/15) **Complete**

Q4. Complete initial carbon-SEI interfacial studies (9/30/15) **Complete**

Go/No-Go: Determine whether NMR has the sensitivity to probe organics on the cathode side in paramagnetic systems (9/30/15) **Stopped project temporarily**

2015

Q1 Identify the major carbon-containing break down products that form on graphene platelets. **Ongoing.** Decision made to complete Si studies (Q3 milestone) first since student is graduating

Q2 Establish the difference between extrinsic and P-doped silicon nanowires **Ongoing**

Q3 Complete SEI study of silicon nanoparticles by NMR spectroscopy. **Complete** Develop NMR methodology to examine cathode SEI **Ongoing**

Q4 Produce first optimized coating for Si electrode. **On track**

Approach/Strategy

- **Optimizing Si performance**
  - Structures formed on cycling
  - Reducing overpotential
  - Building a better SEI

- **SEI studies**
  - NMR studies of local structure as a function of cycling
  - 2 dimensional and double-resonance NMR studies to establish proximity between species

- Development of new platform for *in situ* studies.
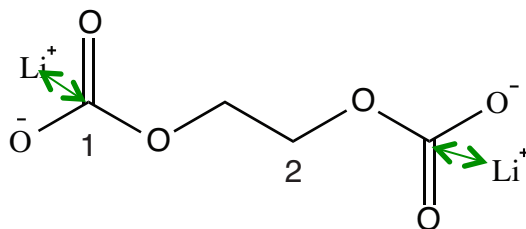- ^{6,7}Li NMR studies of structure
- NMR and electrochemical studies of Si coatings/surface treatments

- ^{13}C NMR studies of ^{13}C-enriched electrolytes to study SEI organic components; ^{7}Li, ^{19}F and ^{31}P studies of inorganics
- ^{13}C NMR studies of reduced VC and FEC additives with naphthalene (B. Lucht)
- Develop new coating strategies and chemistries (D. Wright, E. Eiser)

- MRI studies to correlate electrolyte concentration gradients with dendrite formation

e.g., ^{7}Li -> ^{13}C CP to detect C nearby Li

LEDC

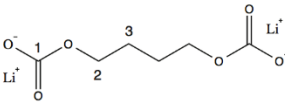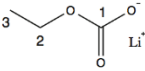# Technical Accomplishments and Progress
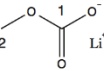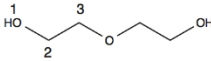
1. Silicon SEI
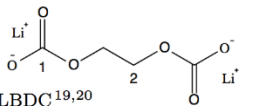
First Studies Used Binder Free System – to remove ^{13}C background and produce *more* SEI

Voltage Dependent Composition of the SEI:

**Use DFT Methods to Provide Estimates for $^{13}C/^{1}H/^{7}Li$ NMR Shifts of Predicted Products and Functional Groups:**
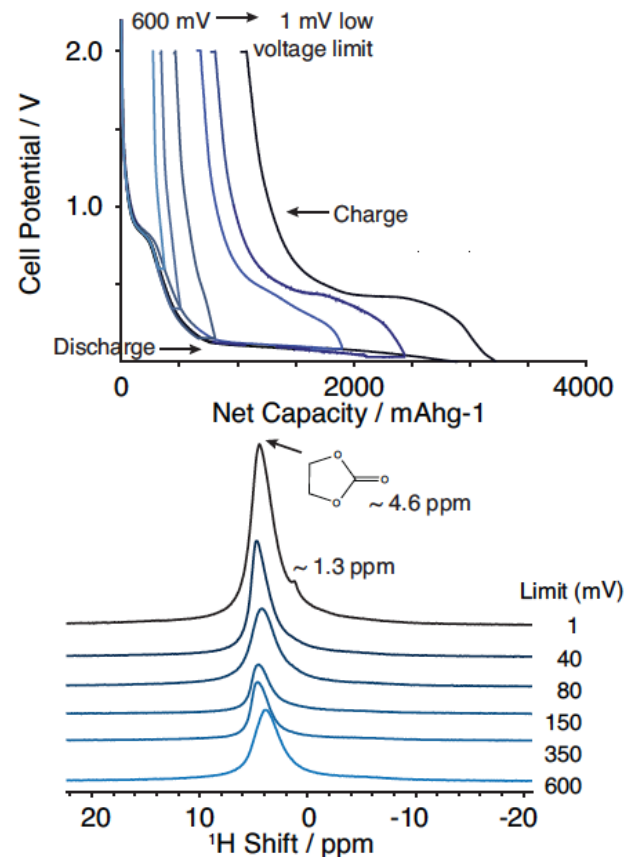
Molecule	Atom	Calculated and Measured Chemical Shifts / ppm		
		ChemNMR	DFT	Experimental
LEDC				(solvent: AC-d$_6$[9]/D$_2$O[7])
	C1	161	171.0	157/161.2
	C2	65.5	64.5	62.9/62.5
	H2	4.39	4.3	3.53/3.51
	Li	-	0.9	
LBDC [19,20]				
	C1	161	171.3	
	C2	67.1	68.0	
	C3	24.8	25.4	
	H2	4.21	4.1	
	H3	1.61	1.7	
	Li	-	1.0	
LEC				(solvent: D$_2$O[8])
	C1	161	171.4	163.7
	C2	63.5	62.8	60.1
	C3	13.8	11.9	19.4
	H2	4.21	4.1	3.65
	H3	1.27	1.5	1.17
	Li	-	1.0	
LMC				(solvent: AC-d$_6$/DMSO[9]/D$_2$O[8])
	C1	161	171.9	160.97/157.02/163
	C2	54.1	51.5	62.40/51.51/54.6
	H2	3.68	3.8	3.56/3.27/3.35
	Li	-	0.9	na
PEO				
	C2	61.3	62.5	
	C3	70.3	70.9	
	H1	5.4	0.1	
	H2	3.7	4.0	
	H3	3.54	3.7	

^{1}H NMR: New species at 1.3 ppm (saturated CH groups) emerges at lower voltages
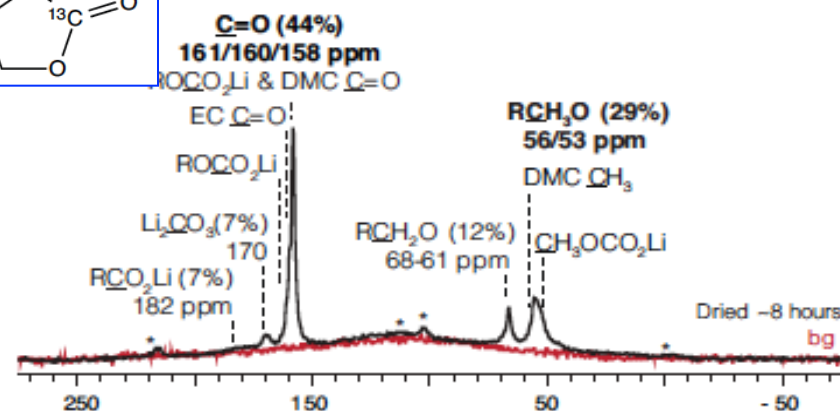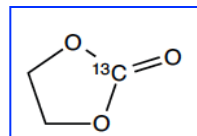
Composition of the SEI on Silicon after 1 cycle

- Detailed ^{13}C measurements of selectively labeled molecules yield composition of organics
  High concentration of EC trapped in SEI
- Li-> C CP detects lithiated carbonates ($ROCO_2$-) , Li_2CO_3, formates (H- and RCO_2Li)
- A number of ether carbons from EC/DMC decomposition products are detected beneath the EC resonances

^{13}C-enriched EC

DMC

(A) $^{13}C_3$ EC Sample   (B) $^{13}C_1$ EC Sample   (C) $^{13}C_3$ DMC Sample
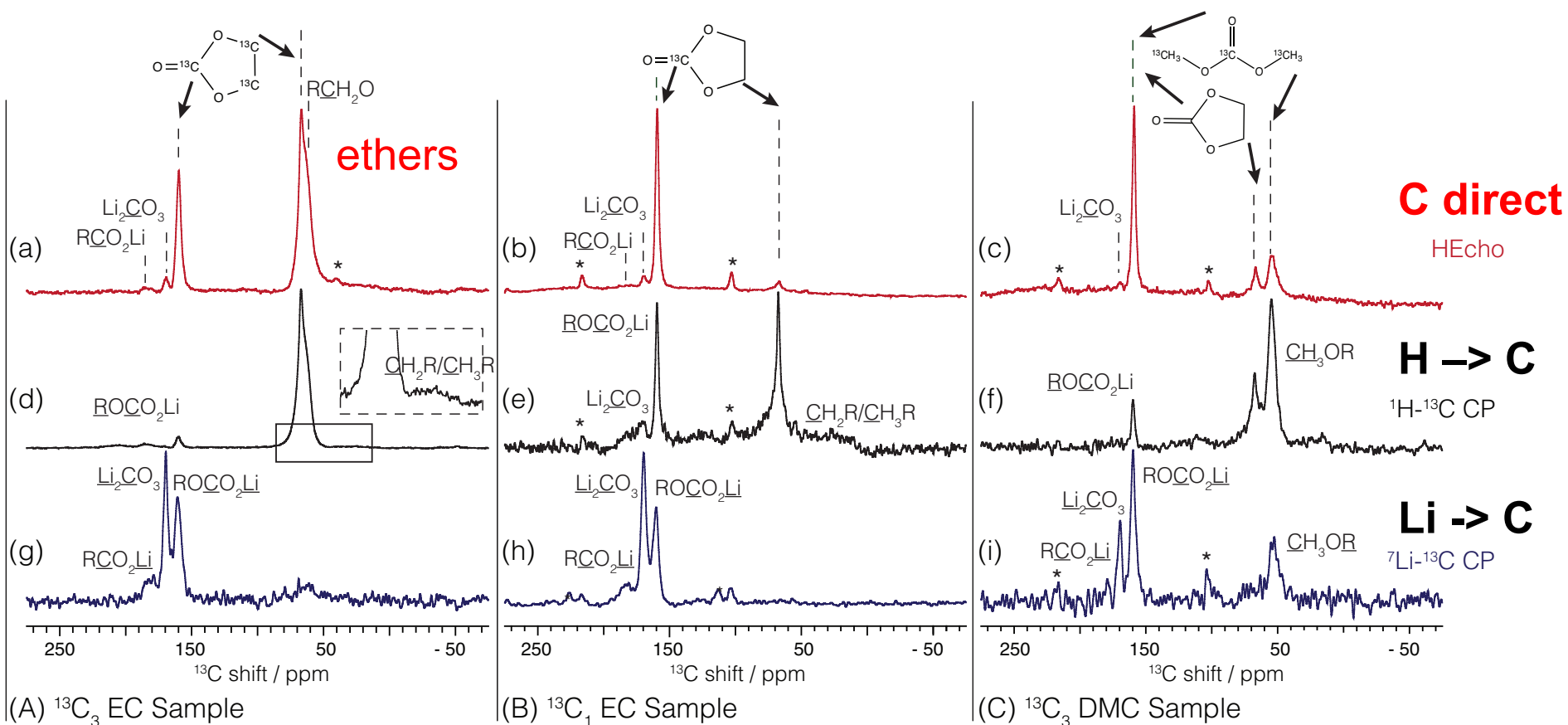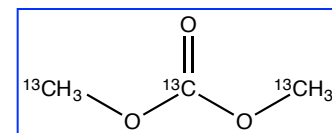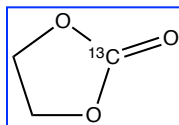
Quantification of the signals/species

Proposed Decomposition Products	Total ^{13}C Signal (%)	Molecular Ratio
(a) $^{13}C_3$ EC Sample		
PEO $-OCH_2CH_2O-$	51	25
LEDC $(CH_2OC_2Li)_2$	28	7
LEC $CH_3CH_2OCO_2Li$	18	6
and LBDC $(CH_2CH_2OCO_2Li)_2$		
RCO_2Li	2	2
Li_2CO_3	1	1
(b) $^{13}C_3$ DMC Sample		
LMC CH_3OCO_2Li	58	29
Non-labelled EC and products	27	
RCO_2Li	7	7
Li_2CO_3	7	7
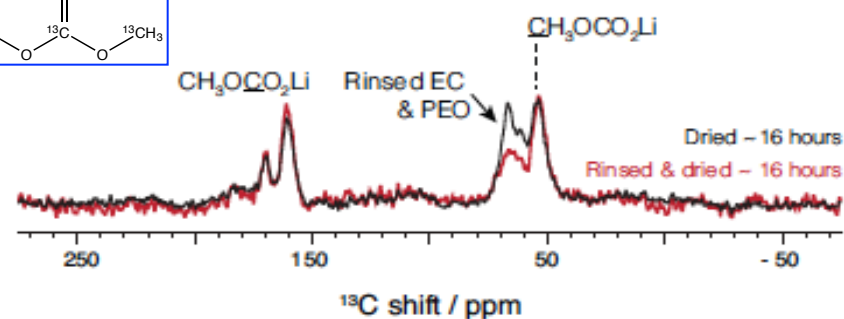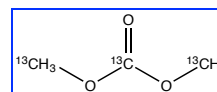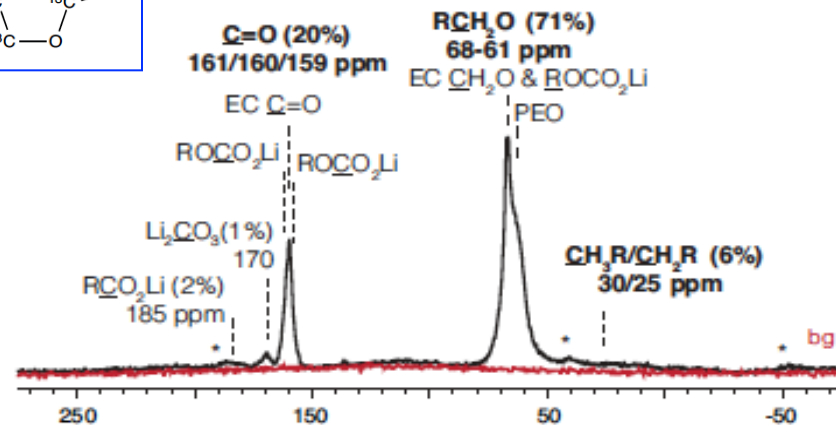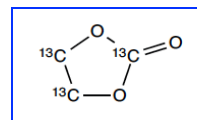
Proposed Decomposition Mechanisms of EC & DMC

PEO

LEC

LEDC

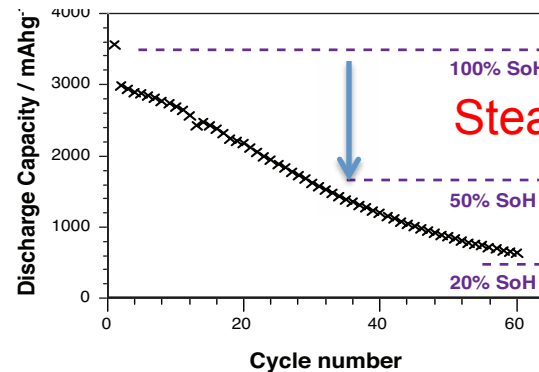**LBDC**

and/or + CH$_2$=CH2 ↑
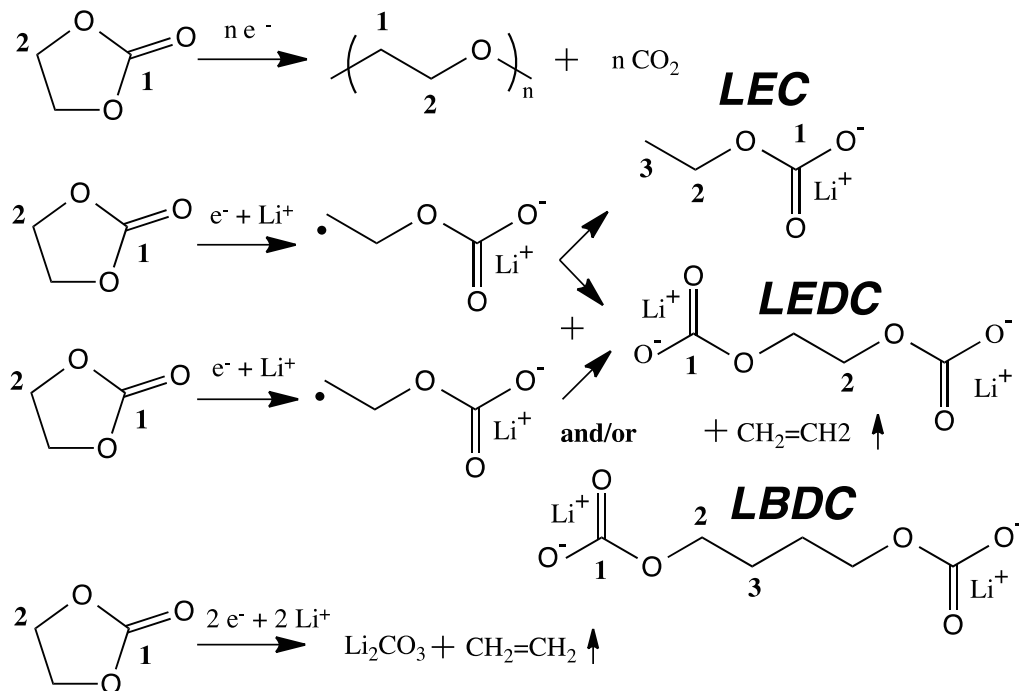
Our results showed experimental evidence of decomposition products, consistent with theoretically predicted reduction mechanisms.

LEDC is widely believed to be an important EC decomposition product. We also observe evidence for LBDC and LEC (CH$_2$R/CH$_3$R ~ 30/25 ppm, C3).

Note that:
- some CH$_2$(/CH$_3$)CH$_2$-O comes from DMC reactions *not* described above
- ^{1}H NMR suggest that these species are formed during the low V plateau

PEO species dominate EC decomposition products..

Chem Mater 2016

"Extended" cycling with CMC
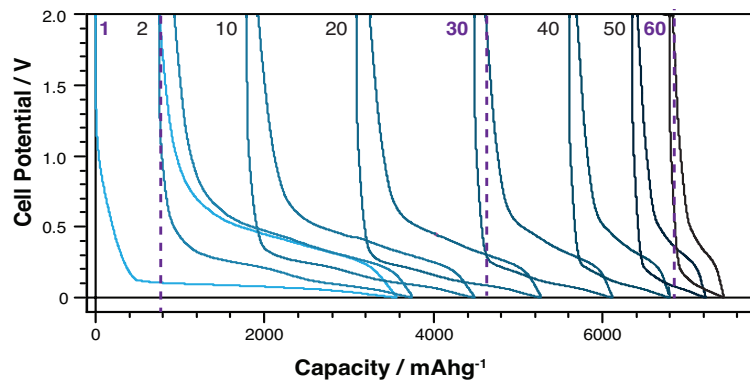
Steady growth in SEI

No distinct difference seen by NMR

No SiO$_y$F$_x$

(a) ^{13}C-labelled EC

Cycle 60
Cycle 30
Cycle 1

(b) ^{13}C-labelled DMC

Cycle 60
Cycle 30
Cycle 1
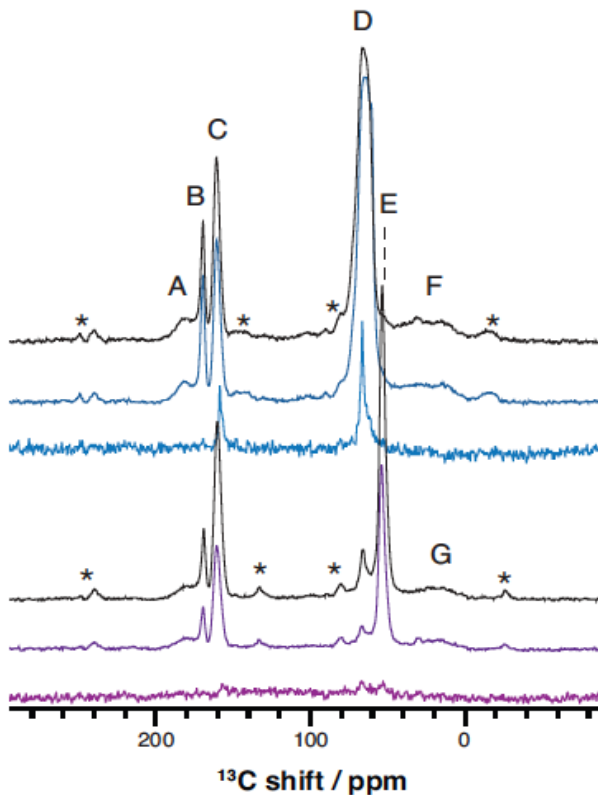
Minor organics on 1st cycle
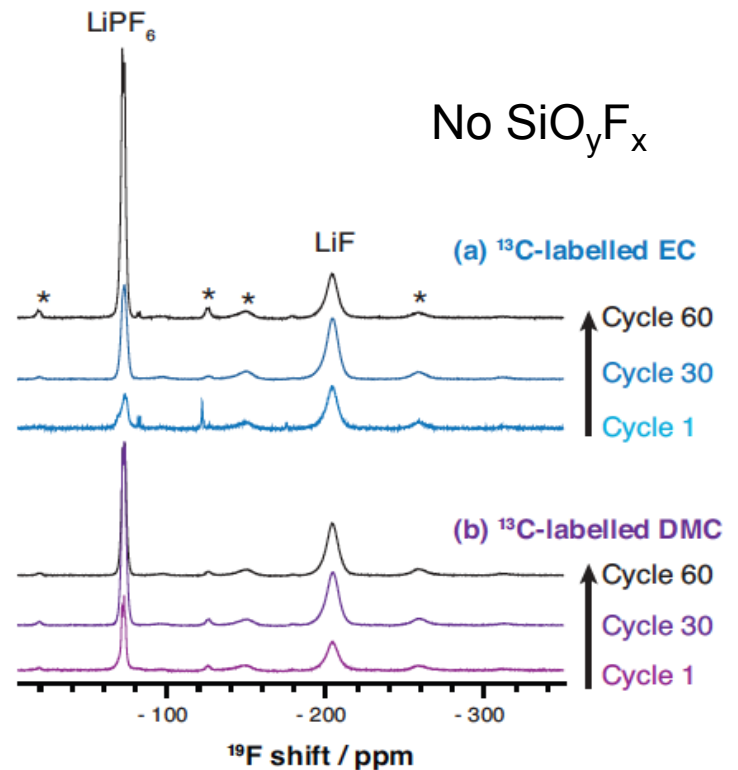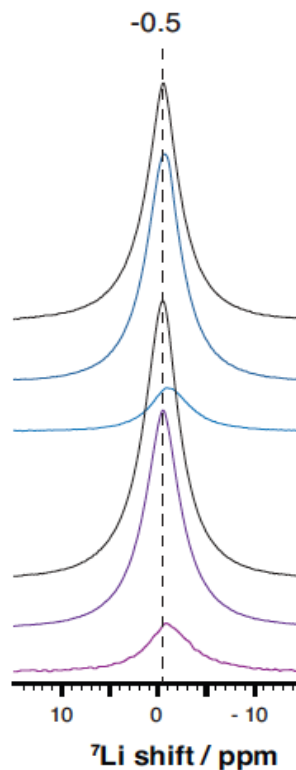
Significant LiF on 1st cycle

Identification of longer chain organics

2D correlations between **bonded carbon atoms**
(CMC, 15 cycle sample)
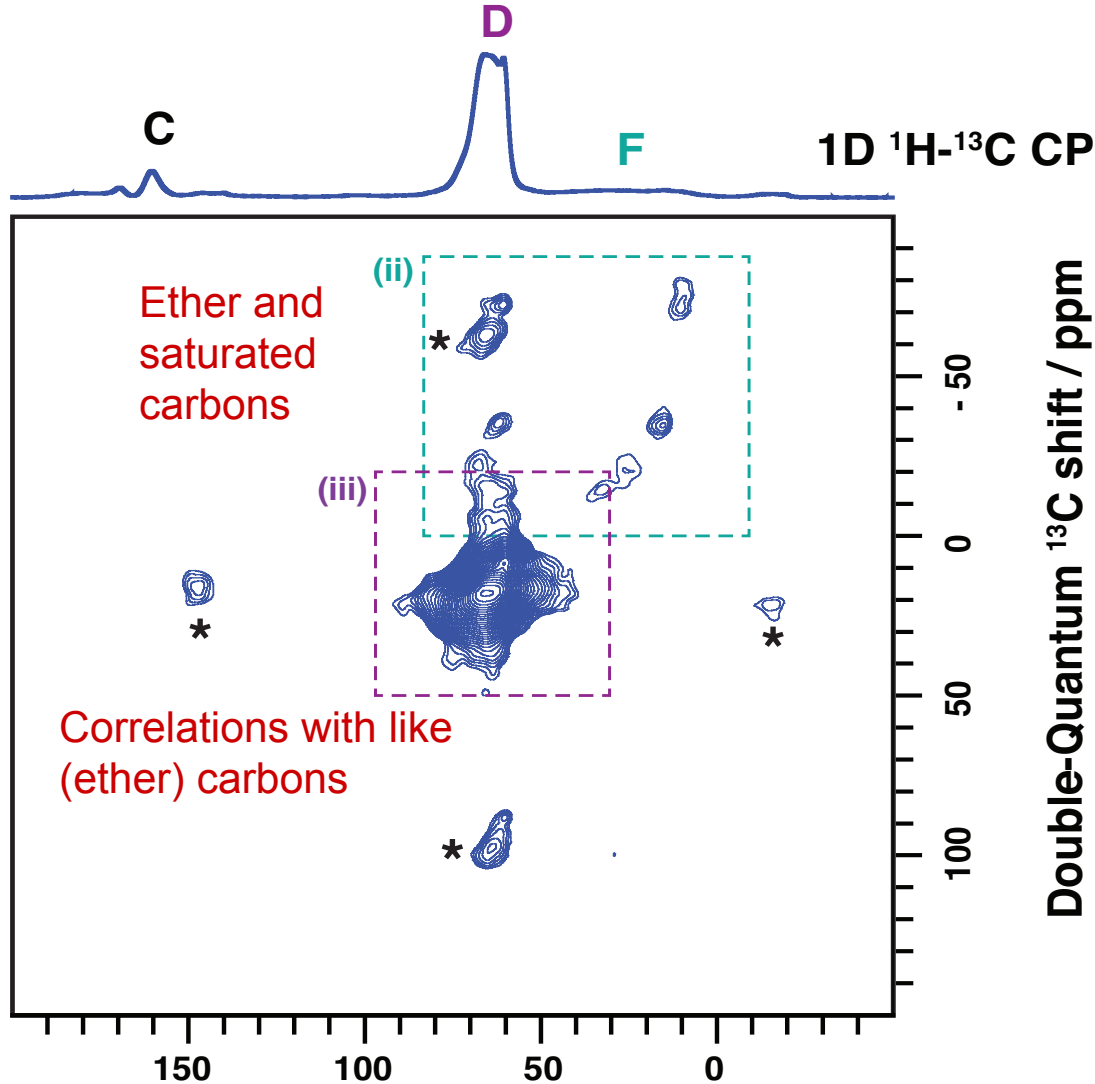
Identification of longer chain organics

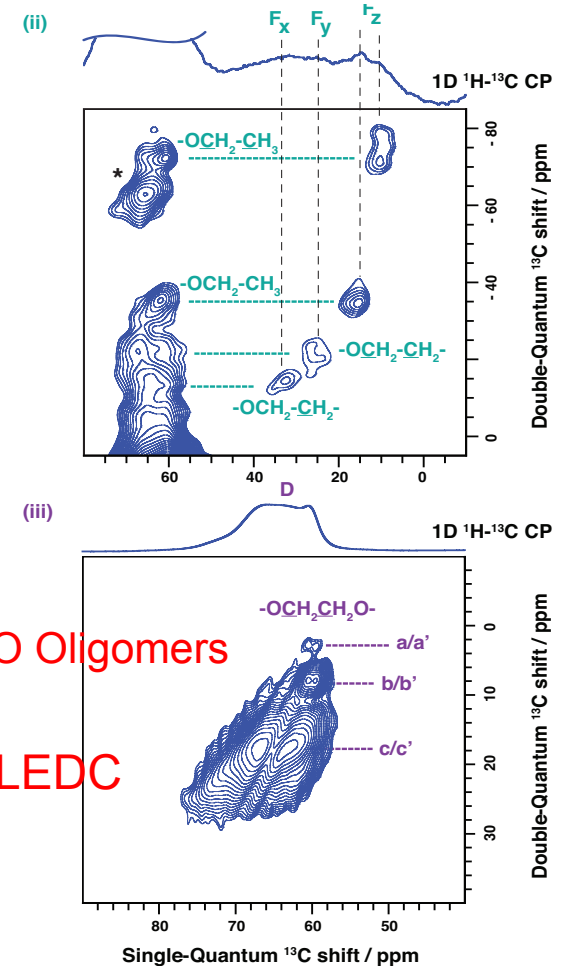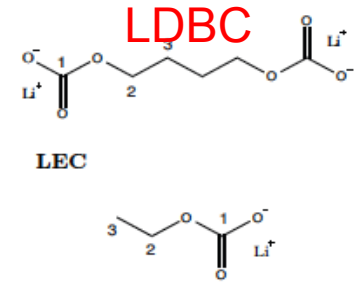| Resonance		^{13}C Shift/ppm	Fragment
A:	EC/DMC	179	$R\underline{C}O_2Li$, $H\underline{C}O_2Li/CH_3CH_2\underline{C}O_2Li$
B:	EC/DMC	170	$Li_2\underline{C}O_3$
C:	EC/DMC	160	$RO\underline{C}O_2Li$, residual EC/DMC $\underline{C}=O$
D:	EC/DMC	67	$\underline{R}OCO_2Li$, residual EC $\underline{C}H_2$, PEO $-O\underline{C}H_2\underline{C}H_2O-$
E:	DMC	53	CH_3OLi residual DMC CH_3
F_x:	EC	30	$R\underline{C}H_2R'$
F_y:	EC	23	$CH_3\underline{C}H_2R$
F_z:	EC	14	$\underline{C}H_3R$
G_x:	DMC	30	$R\underline{C}H_2R'$
G_y:	DMC	23	$CH_3\underline{C}H_2R$
G_z:	DMC	14	$\underline{C}H_3R$

Assignments for the ^{13}C spectra of the 15 cycle sample

Pristine

30 cycles

60 cycles

Cycling with CMC

Cycle 2-30: Uniform lithiation

a-Si → a-Li$_x$Si → a-Li$_{(x+x')}$Si
2 V   250 mV   100 mV

Cycles 30-60: Surface particle lithiation

a-Si → a-Li$_x$Si + a-Si → a-Li$_{(x+x')}$Si + a-Li$_x$Si + a-Si
2 V   250 mV   100 mV

Current Collector
Li Metal Counter Electrode
Separator & Electrolyte

Si/CMC/C Electrode
(FIB/SEM)

Current Collector

Li$^+$
SEI

Li$^+$ ion diffusion through entire porous electrode structure

Li$^+$ ion diffusion restricted to surface regions near separator and of large voids due to SEI delamination and dense electrode structure.

Li$^+$ ion diffusion in the increasingly dense electrode structure: expansion on lithiation reduces transport through top of electrode

Capacity loss and evolving kinetics: high voltage process lost due to increased tortuosity through electrode

Cycle 2   Cycle 30   Cycle 60

↑ Charge
↓ Discharge

Cell Potential / V

Capacity / mAhg^{-1}

Differential Capacity dQdV^{-1} / mAh^{-1}g^{-1}V^{-1}

a-Si 2V

a-Li$_x$Si 250 mV

a-Li$_{(x+x')}$Si 100 mV

Capacity loss from high voltage process

Some capacity from low voltage process

Decreasing intensity of high voltage process

Restricted Li$^+$ diffusion forces low voltage process in surface particles
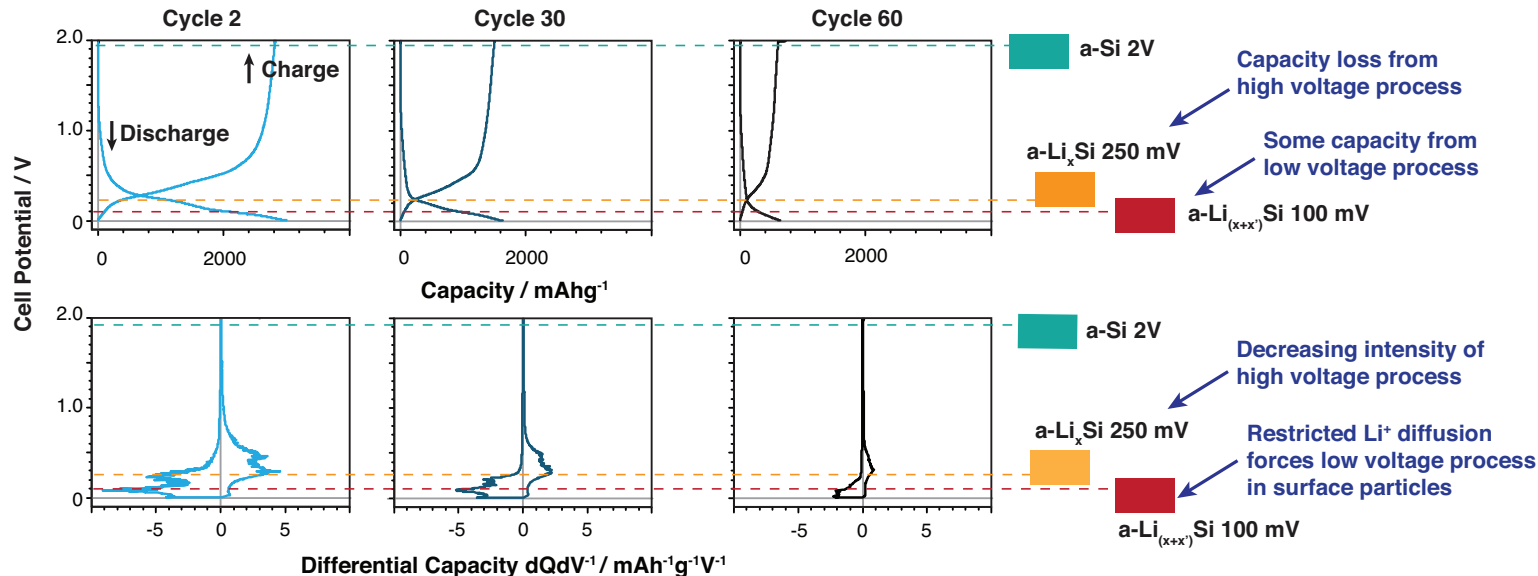
Correlating Dendrite Formation with Concentration Gradients: MRI Studies

High current (0.76 mA cm^{-2})

(a) Pristine (b) t = 10.5 hours (c) t = 18.6 hours (d) t = 32.7 hours

Low current (0.16 mA cm^{-2})

(a) Pristine (b) t = 23.1 hours (c) t = 52.8 hours (d) t = 73.1 hours
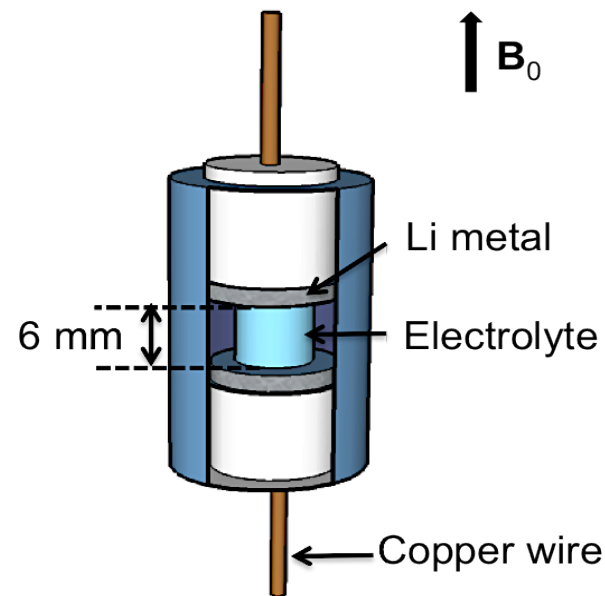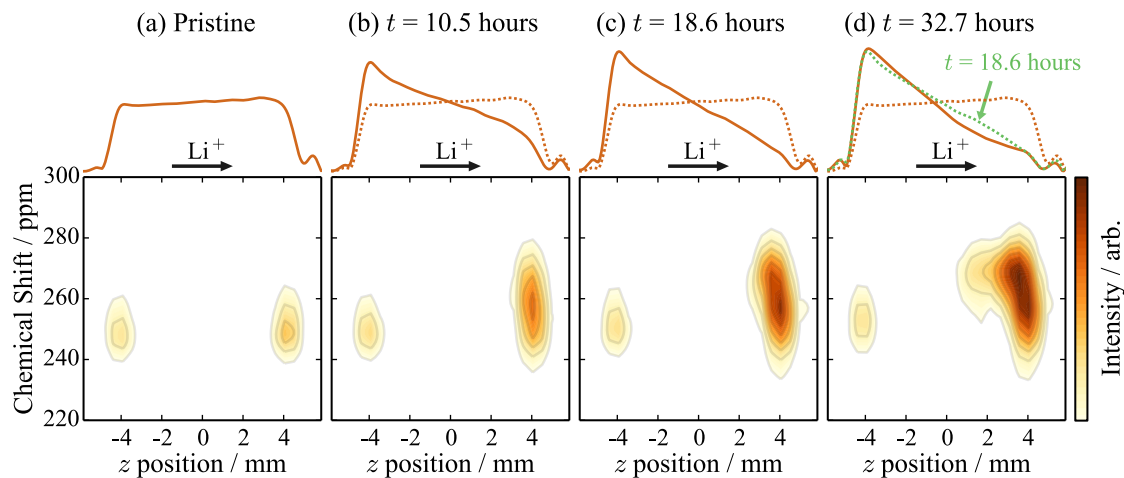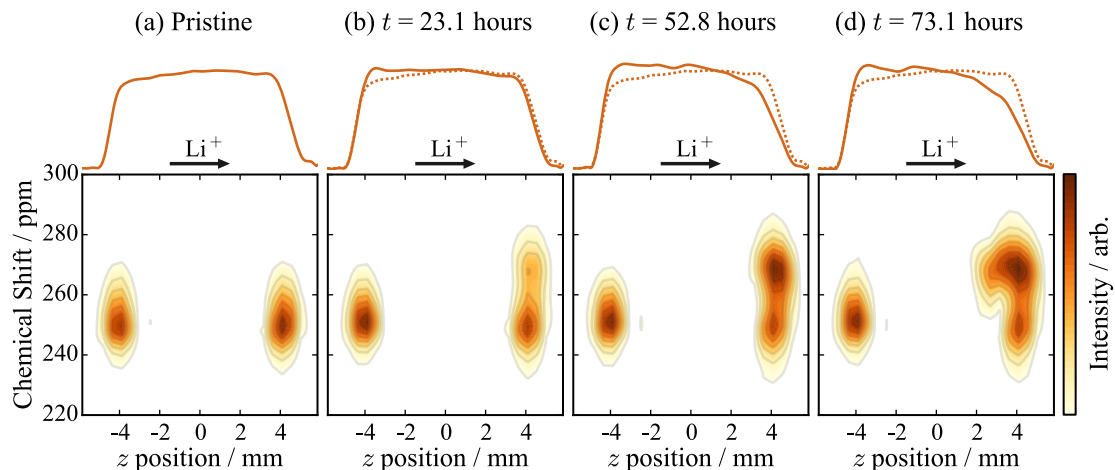
With A. Jerschow, NYU

c.f. M. Klett, M. Giesecke, A. Nyman, F. Hallberg, R. W. Lindstrom, G. Lindbergh and I. Furo, *JACS*, 2012, **134**, 14654-14657.

Correlating Dendrite Formation with Concentration Gradients: MRI Studies
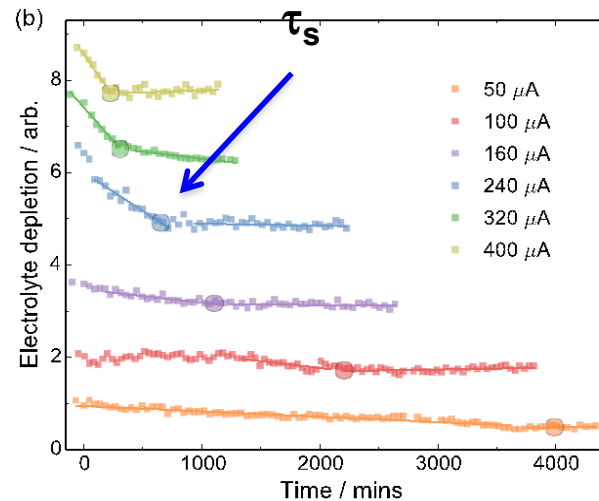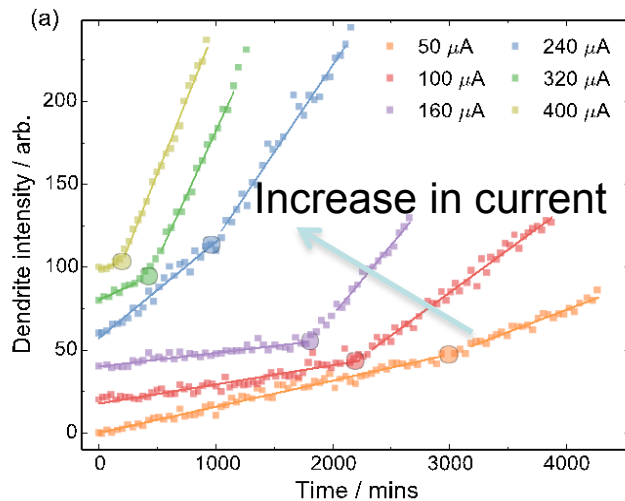
Sands time, τ_s

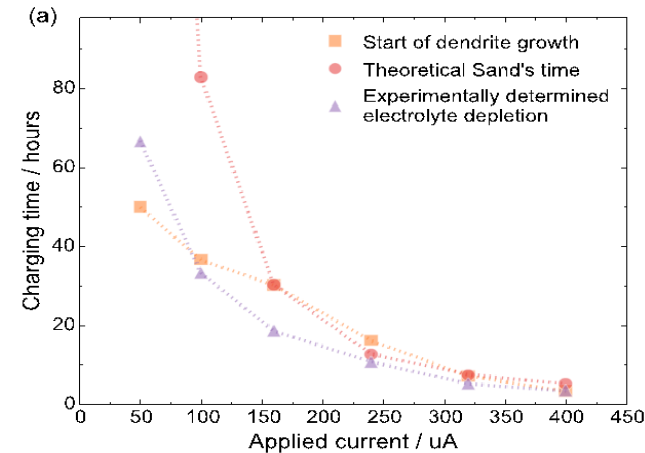Time the anion concentration at the anode drops to zero (@ high current densities) Electroneutrality breaks down and dendrites grow from anode

$$\tau_s = \pi D \left(\frac{C_0 e}{2J t_a} \right)^2$$

C_0 = initial electrolyte concentration
t_a = transport no. of anion
J = Current density
D = ambipolar diffusion time

J.-N. Chazalviel, *Phys. Rev. A*, 1990, **A 42**

NMR Sands Time?

Two mechanisms for microstructure growth clearly seen

•High currents – Sands time mechanism holds
•Low currents – Transition to dendritic structure still occurs- local Li depletion @ SEI/Li interface?
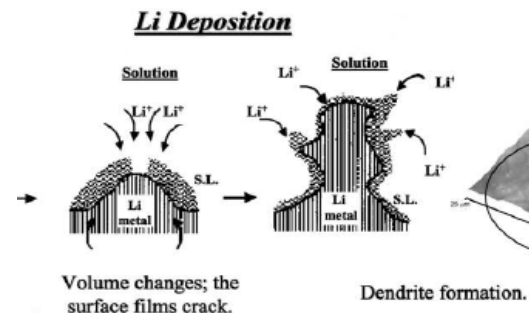
Role of additives and electrolyte?

D. Aurbach et al. SSI (2012)

Li air chemistries in the presence of H₂O and LiI additives cycle via the formation of LiOH – not Li₂O₂
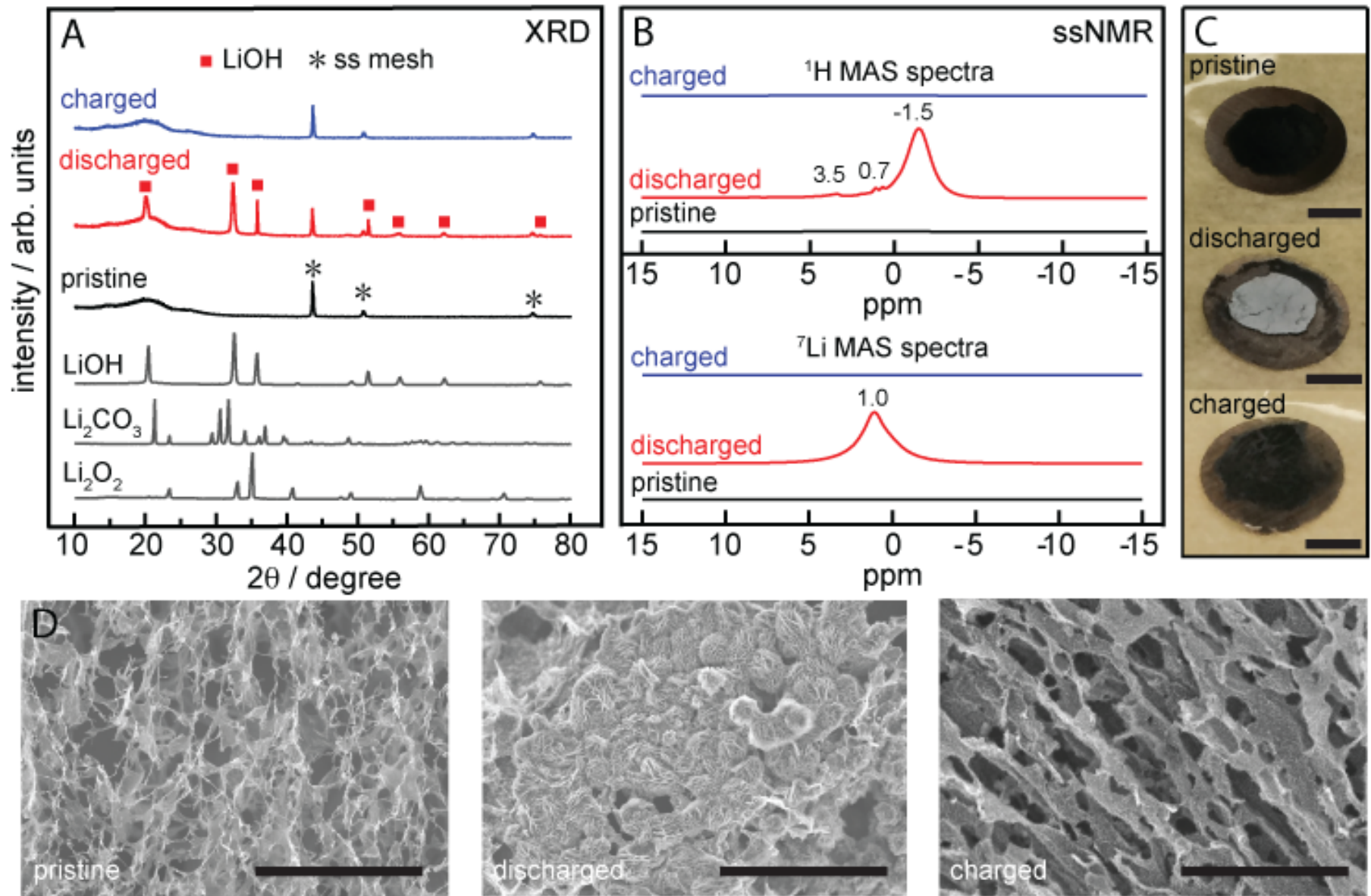
Responses to Previous Year Reviewers' Comments

- The reviewer's comments were generally extremely positive, Reviewer 3 noting that "Clare Grey's nuclear magnetic resonance (NMR) work and method development seemed truly groundbreaking" and Reviewer 2 saying that "those developing new methods seem to be rushed to apply them to lots of materials right away, presumably to show relevance and highlight the importance of the work. The reviewer fears the project teams are rushing into the application field too quickly, before the teams have really done a thorough job of validating the method. The reviewer was happy to see that Clare Grey's group took a time-out to look at their methods in such detail."

- In response to Qu 1, reviewer 2 stated "The only aspect the reviewer would question is the breadth of studies conducted under this effort, which the reviewer noted is attacking a lot of very difficult problems."
  In response to this we stress that the major focus of this project is and continues to be the SEI. However, we continue push the use of our in-situ metrology to examine different, relevant battery chemistry, to expand the applicability of the method, to learn increasingly new and varied information from a wider class of battery systems and materials.

- Reviewer 3 stated "Li-ion conductivity in SEI should be investigated using NMR, and noted that no study on electrode tortuosity was reported." We agree, and these studies are in progress. To this end we have performed FIB SEM studies of electrode morphology, and PFG/MRI/tomography experiments are in progress. The conductivity studies (by NMR) are more challenging and we will seek to develop approaches to this within the coming year (i.e., before the termination of the current funding cycle).

- Reviewer 1 "described the future planned work as very ambitious", while Reviewer stated that "The Si SEI work is excellent and highly relevant, .. referring to earlier comments on whether the Si SEI is truly passivating. Another valuable focus, in this reviewer's opinion, would be trying to understand the effect of additives, such as FEC, on the SEI makeup. The reviewer was unsure about the purpose of the Na dendrite study, because Na offers no obvious benefit for transportation applications, in the reviewer's view."
  The FEC/VC work is on going the challenge for NMR being the difficulty in enriching these materials in ^{13}C. We have worked with Prof. B Lucht to prepare and characterize bulk reduced FEC and EC and a paper describing this work is about to be submitted. We are developing approaches to examine FEC/VC systems and we hope to report on this later on in the year. With respect to the Na work, we stress that this was part of the *in situ* metrology development and the study led to insight into the nucleation and growth of dendrites that has value for the LIB chemistry as well.

Collaboration and Coordination with Other Institutions

- Brett Lucht* (Rhode Island) – SEI and additives; provided reduced FEC/VC samples (BMR)

- Elizabeth McCord, Bill Holstein (DuPont) – input on SEI and electrolytes

- Jordi Cabana* (UIC); Stan Whittingham* (Binghamton), Shirley Meng*, Peter Bruce - Na cathodes (samples, magnetism)

- Stephan Hoffman, Cate Ducati, Andrew Morris (U. Cam) – Synthesis of Si nanowires, TEM, theory (Si)

- Dominic Wright, E. Eiser (U. Cam), new electrode coatings

- Paul Shearing (UCL) – X-ray tomography

*BMR collaborators

Remaining Challenges and Barriers

- SEI studies are time consuming because the small sample sizes (poor S/N in NMR) and moisture/air sensitivity issues (cannot keep samples for long period of times).– comprehensive study takes time!

- Cannot simply obtain ^{13}C enriched FEC/VC – need to rely on ^1H and ^{19}F studies.

- Sensitivity of NMR studies to study thin cathode SEI (CEI) - DFT studies to help assign spectra. Development of new NMR experiments for use at higher fields (increase sensitivity)

- Tortuosity measurements by magnetic resonance: difficult on highly paramagnetic/metallic samples, limited resolution of MRI experiments means thick samples need to be prepared. Continue on graphites and Si. Explore very low field measurements. Have now built relevant e-chem cells

18

Proposed Future Work

- Complete graphite/graphene SEI study
- Continue Si-coating studies; investigate SEI in presence of coatings
- Continue tortuosity PFG and MRI experiments with focus on graphite and Si electrodes.
- Investigate effect of additives and different electrolytes on Li dendrite growth
- Complete (Ni,Mn)O Na-layered materials study
- Investigate catalytic OER reactions in the Li-air system

Summary

Silicon SEI:
- Selective labeling and a series of 1 and 2D NMR experiments have been used to identify a series of products in the SEI.
- Correlations identify species in close proximity (e.g., Li---X and C – C connectivity).
- PEO-type oligomers are in high abundance – some are removed on washing indicating that they are in the fragile/organic more porous part of the SEI
- LiF, Li_2CO_3, RCO_2Li are seen in addition to the semicarbonates LMC, LEDC, LBDC and LEC
- SEI growth is voltage dependent – and a new local environment (with saturated groups as expected in LBDC and LEC) is observed @ very low voltages
- Some evidence that some saturated CH_3 groups are formed from DMC in addition to EC.
- Same species seen with CMC binder – but organic SEI formation much slower – LiF formed on 1st cycle; very little growth thereafter

Li Dendrites:
- Two mechanisms for microstructure growth clearly seen
- High currents – Sands time mechanism holds – dendrites grow when electrolyte depletion near current collector observed
- Low currents – Clear transition from mossy Li to dendritic growth is still observed. Thick SEI causes electrolyte depletion near Li metal?
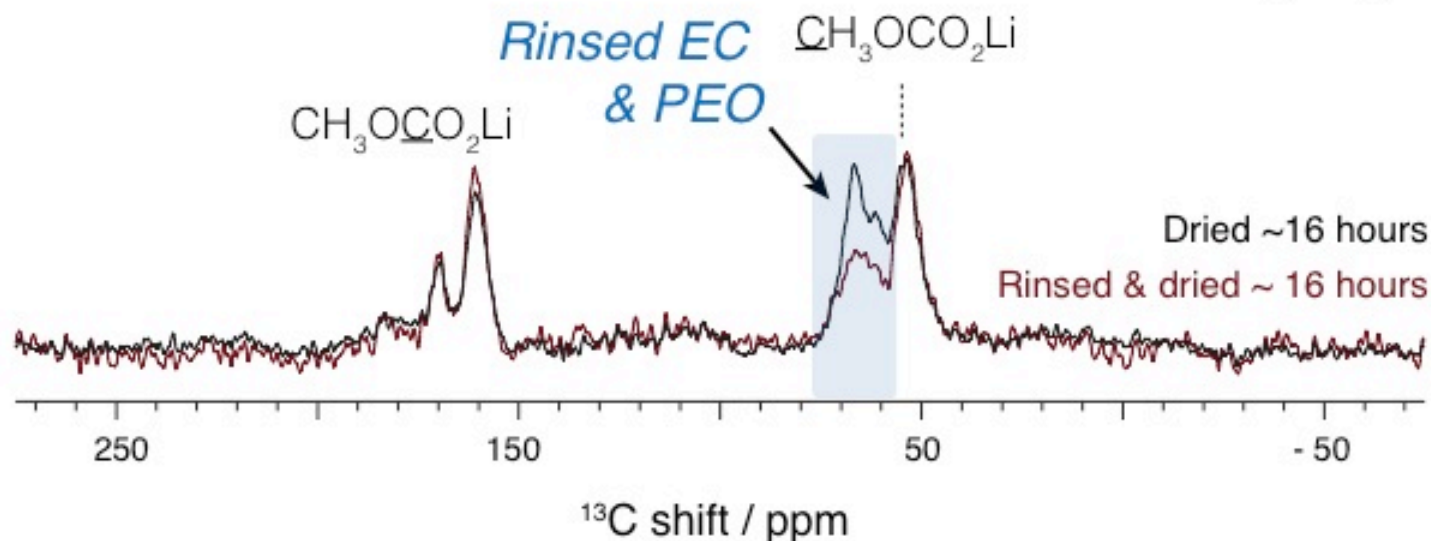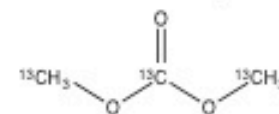
Li Air:
- LiOH formed in the presence of LiI additives, the protons coming from added H_2O and not the electrolyte (DME).
- Reversible chemistry seen over multiple cycles indicating that LiOH can be removed

Technical Back-Up Slides

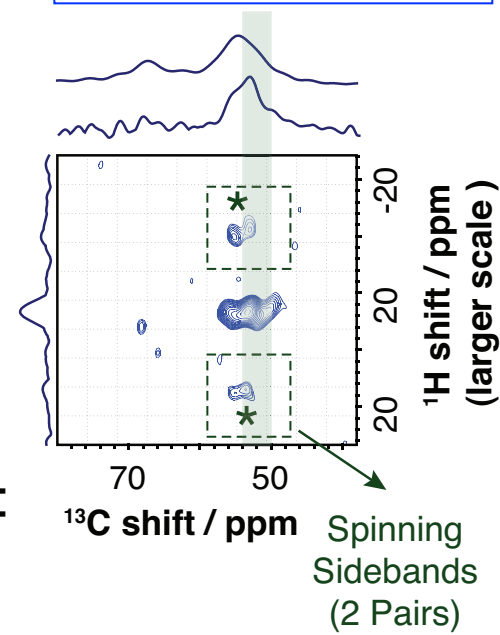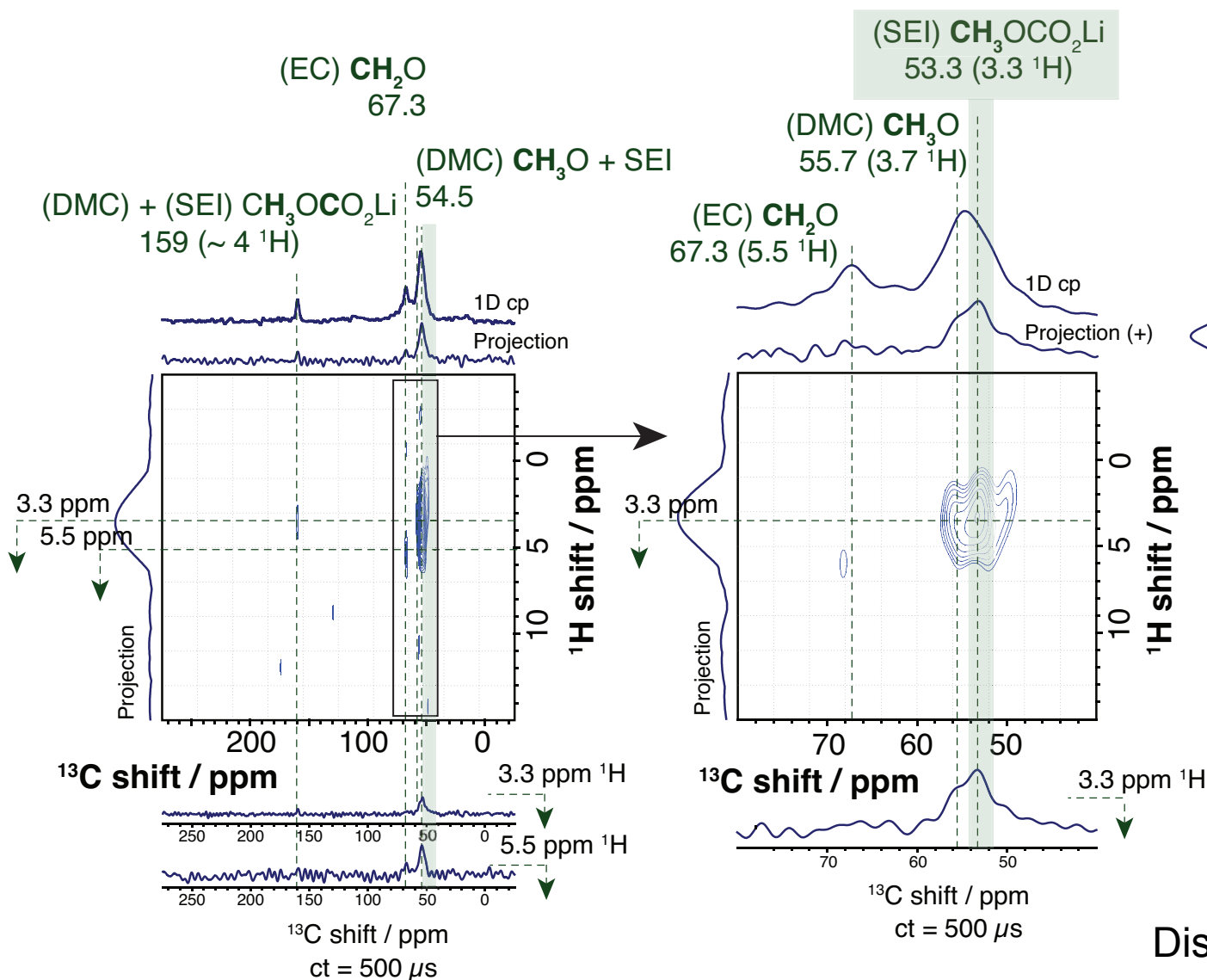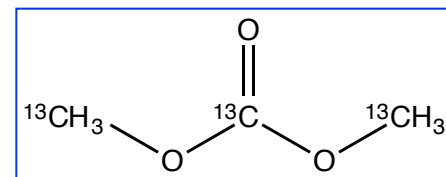# Investigation of the organics in the SEI: structural information

Rinsing electrode samples to remove excess electrolyte is a commonly used technique for ex-situ SEI studies.

Our preliminary rinsing studies suggested PEO-type organics are removed by rinsing. These fragile organics are likely on the outermost layer of the SEI.

Use 2D experiments to help assignments:
E.g., ^{13}C-^1H Correlation NMR Experiments with enriched DMC

(EC) **CH$_2$**O
67.3

(DMC) **CH$_3$**O + SEI
54.5

(DMC) + (SEI) C**H$_3$**OCO$_2$Li
159 (~ 4 ^1H)

(SEI) **CH$_3$**OCO$_2$Li
53.3 (3.3 ^1H)

(DMC) **CH$_3$**O
55.7 (3.7 ^1H)

(EC) **CH$_2$**O
67.3 (5.5 ^1H)

1D cp

Projection

3.3 ppm
5.5 ppm

^1H shift / ppm

^{13}C shift / ppm

3.3 ppm ^1H
5.5 ppm ^1H

^{13}C shift / ppm
ct = 500 μs

1D cp

Projection (+)

3.3 ppm

^1H shift / ppm

^{13}C shift / ppm

3.3 ppm ^1H

^{13}C shift / ppm
ct = 500 μs

^1H shift / ppm
(larger scale)

^{13}C shift / ppm

Spinning
Sidebands
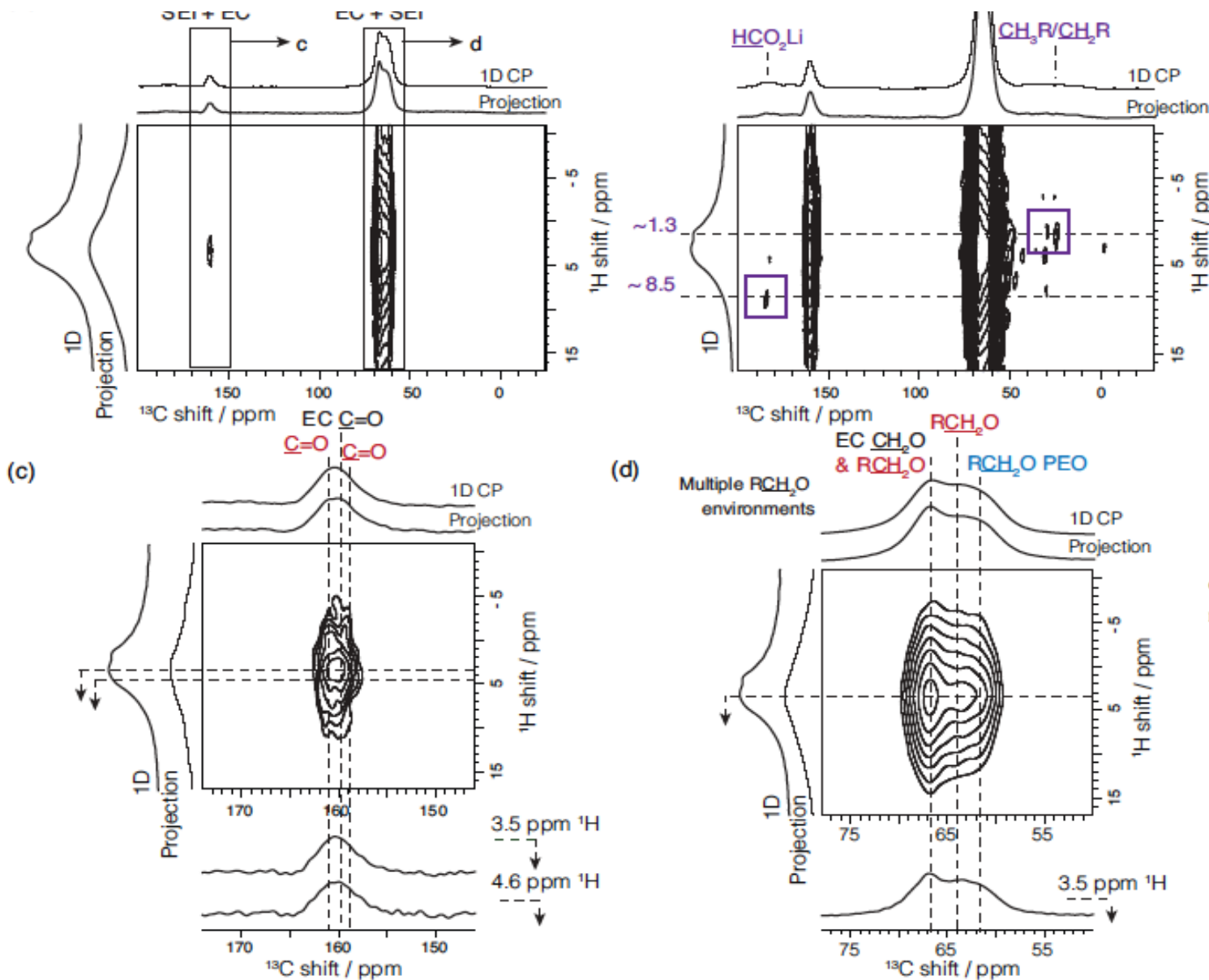(2 Pairs)

At least one DMC
product
CH$_3$-O-CO$_2$-

Distinct from EC products

¹³C-¹³C Correlations: EC products
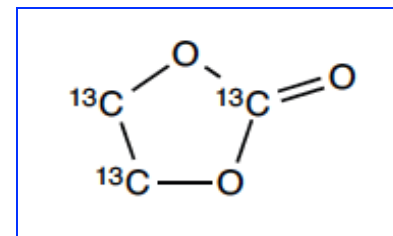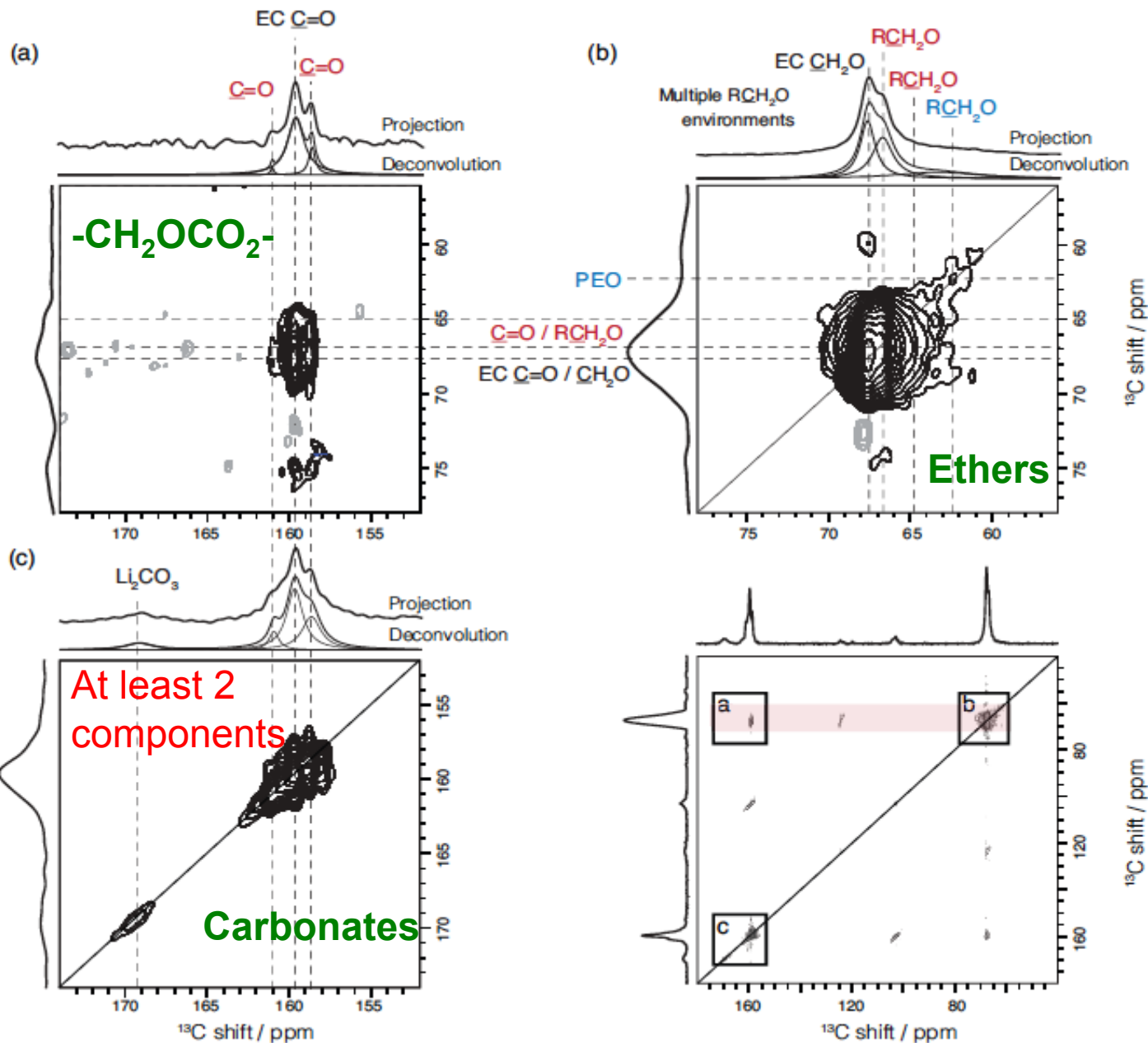
Correlate ether and carbonate regions to separate components

^{13}C-^{1}H Correlation NMR Experiments – EC Products

Formates and CH$_x$CH$_2$-O seen

CH$_x$ seems to come from both EC and DMC